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Effect of Electrolytes and Surfactants on Thai Starch Gel Base

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Objectives

1. To study the physicochemical properties of developed gel base from modified Thai starches and compare with imported semi-synthetic polymer.
2. To study of excipients in the drug formulations.
3. To study the effect of electrolytes and surfactants on stability of Thai starch gel bases and semi-synthetic polymer gel base.

Introduction

Most widely used starch materials were developed in the food, pharmaceutical and cosmetic industry (1). When the properties of native starch have been altered, it is called a modified starch. Native starch was first modified in order to improve its functionality for industrial applications. The properties of the modified starches vary depending on the method of conversion prepared in manufacturing process. The texture of starch sometimes changes the physical and/or chemical properties. Chemically modified starches have been developed to overcome the short coming of native starches (water repellence, insolubility or failure of granules to swell and develop viscosity in cold water) extending the usefulness of starch for many industrial applications (2). Recently, many types of chemical such as acid hydrolysis, oxidation, etherification and esterification have attracted much attention (3-5). The modified product has qualities that are essentially different from the original unmodified material, increasing the utility of this material.

In the present study, three kinds of local made starches, glutinous starch, rice starch and tapioca starch were modified according to carboxymethylation with monochloroacetic acid under basic condition using methanol as a solvent. The development of gel base was stared with employing a semi-synthetic polymer, hydroxypropyl methylcellulose (HPMC) as a referential hydrogel base. The developed gel bases obtained from each modified starch, which had nearly viscosity to the model base. The effects of electrolytes and surfactants on the physicochemical and rheologic properties were studied.

Materials

The glutinous starch and rice starch were purchased from Choheng Co., Ltd. Bangkok, Thailand. The tapioca starch was purchased from Sithinun Co., Ltd. Bangkok, Thailand. Calcium chloride, sodium chloride, monochloroacetic acid, hydroxypropyl methylcellulose, sorbitan monooleate 80 and silver nitrate TS were purchased from Fluka Chemie GmbH, Switzerland. The glacial acetic acid was from BHD Laboratory Supplies, English. The polyoxyethylene sorbitan monooleate 80 was purchased from S.K.Trading Co., Ltd. Chiangmai, Thailand. The methanol AR. was purchased from J.T. Baker, USA.

Methods

Preparation of modified starch

The carboxymethyl starches were prepared according to the procedure of Filbert (6). 100 % Methanol and monochloroacetic acid were mixed to the container and then native starch finally with the addition of sodium hydroxide to the container. Subsequently, the container was heated to the reflux reaction at 60 °c for 60 minutes under stirring. After cooling to room temperature, the pH was adjusted to 7.0. The solid residue was then washed with 80 % methanol until it was free of chlorides. It was then filtered and dried at 50 °c. The same procedure was used for all the materials modified.

Preparation of gel base

Using HPMC, as a hydrogel model base started the development of gel base. The developed gel bases obtained from each modified starches, modified glutinous starch (MGS), modified rice starch (MRS) and modified tapioca starch (MTS) which had nearly viscosity to the model gel base, contained 4% (w/w) of HPMC.

Effect of electrolytes and surfactants

The effects of electrolytes and surfactants on the physicochemical and rheologic properties were studied. The concentration of electrolytes, calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were 0.1 to 0.3 % (w/w). And the surfactants, Span 80 and Tween 80 at concentration 3 %, 5 %, 10 % (w/w) was gradually added into the gel bases. The gel bases were investigated physical properties. The rheologic behavior of gels was studied using a Brookfied rotational viscometer, model DV III (Brookfield Co., Ltd., Massachusetts, USA). The used measurement system was searle geometry with a stationary cylindrical cup and rotating cylindrical spindle. The temperature of the system was controlled at 25 °c.

Results and discussion

The gel bases were stared by using HPMC at concentration 4% (w/w) as a hydrogel model base, which was easily administered by syringe equipped with needles of appropriate size. The developed gel bases obtained from each modified starch, which had nearly viscosity to the model base. In this study, it was found that the suitable concentration of gel bases were contained 8 % (w/w) of MGS, 11 % (w/w) of both MRS and MTS (Fig. 2). The viscosity of HPMC and modified starches were about 36,000 to 39,500 cP. (Fig. 1) The results indicated that the rheologic behavior of HPMC and MTS containing gel bases were plastic flow and MRS containing gel base was plastic with thixotropy. However, MGS containing gel base was pseudoplastic with thixotropy.

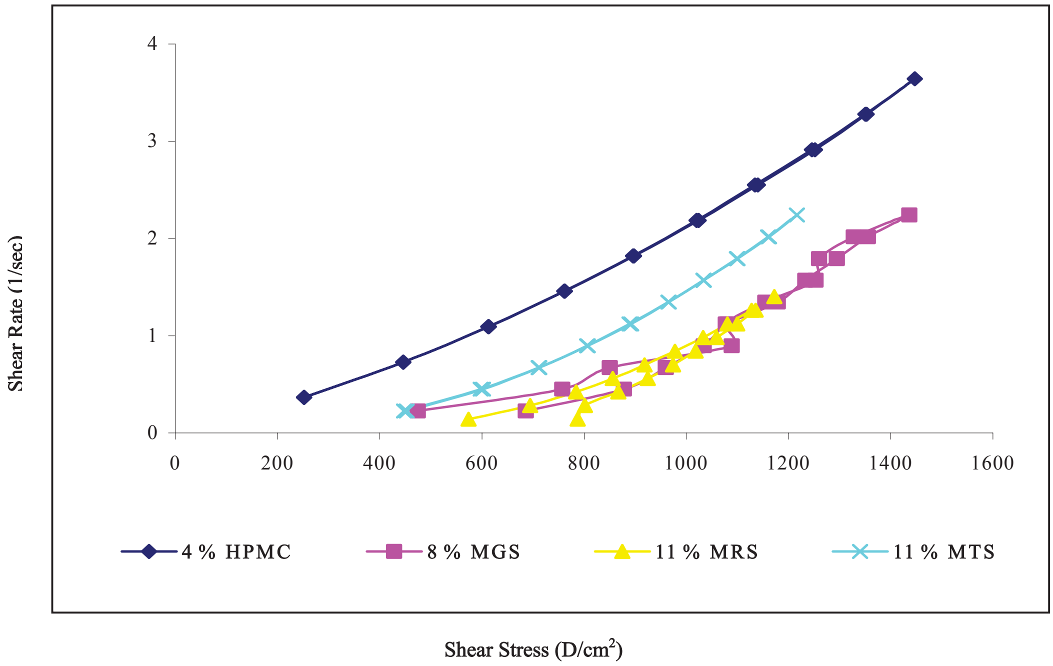

Fig. 1 The evolution of flow curves with times at 25 °c in the presence of gel bases: 4% HPMC, 8% MTS, 11% MRS and 11% MTS

Fig. 2 The image of 4 % HPMC gel base and modified starch gel bases containing 8% w/w MGS, 11% MRS and 11% MTS, respectively.

The effects of electrolytes on the rheologic behavior were studies, which the concentration of NaCl and $CaCl_2$ were 0.1 to 0.3 % (w/w) (monovalent and divalent electrolytes, respectively). The results demonstrate that the electrolytes decreased in viscosity and yield value of modified starches (Fig. 3) and also caused precipitation particularly when high concentration of electrolytes were added. And $CaCl_2$ showed more obviously effect than the NaCl. The results displayed in Fig. 4 showed that higher concentration of $CaCl_2$ is more effective than lower concentration of $CaCl_2$ in the precipitation particularly.

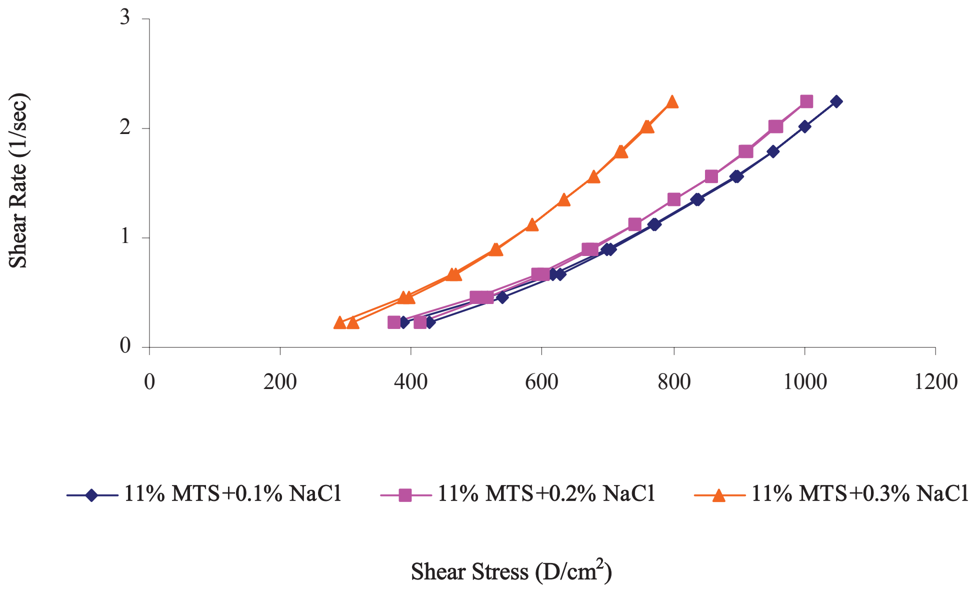

Fig. 3 The effect of NaCl decreased in viscosity and yield value of MTS gel bases

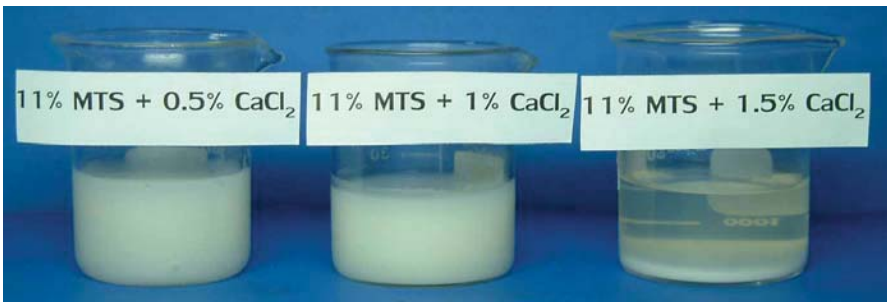

Fig. 4. The effect of added $CaCl_2$ on the precipitation particularly of MTS gel base: 11% MTS + 0.1% $CaCl_2$, 11% MTS + 0.2% $CaCl_2$ and 11% MTS + 0.3% $CaCl_2$, respectively.

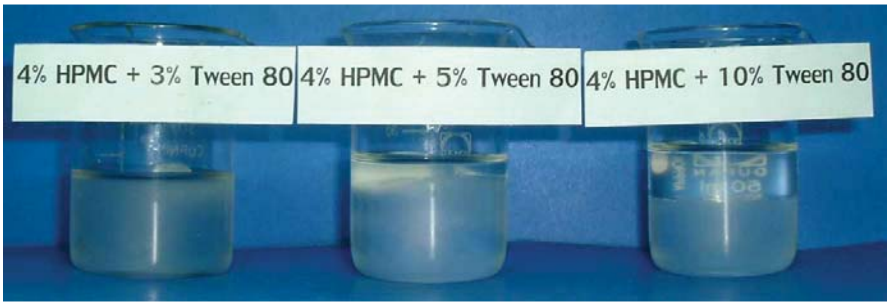

Fig. 5 The effect of added Tween 80 on the precipitation particularly of HPMC gel base: 4% HPMC + 3% Tween 80, 4% HPMC + 5% Tween 80, 4% HPMC + 10% Tween 80, respectively.

In addition, two different nonionic surfactants, a water-soluble Tween 80 and a lipid-soluble Span 80 were added to each gel bases with the aim of improving physical and rheologic properties. The results also indicate that there is the incompatibility between Tween 80 and HPMC gel by causing precipitation in the gel bases (Fig. 5). Rheograms also demonstrate a huge hysteresis loop, particularly in the system that contained Span 80, which appeared as a large bulge in the up-curve (Fig. 6). In addition, gel-to-sol transformation and shear thinning or consistency lost through shearing became less viscous as the shear rate increased, which facilitated the flow of the gel bases. The huge hysteresis loop indicated a breakdown of structure that did not re-form immediately when the stress was removed or released. The results on effect of surfactants indicated that Span 80 demonstrated stronger effect than the Tween 80.

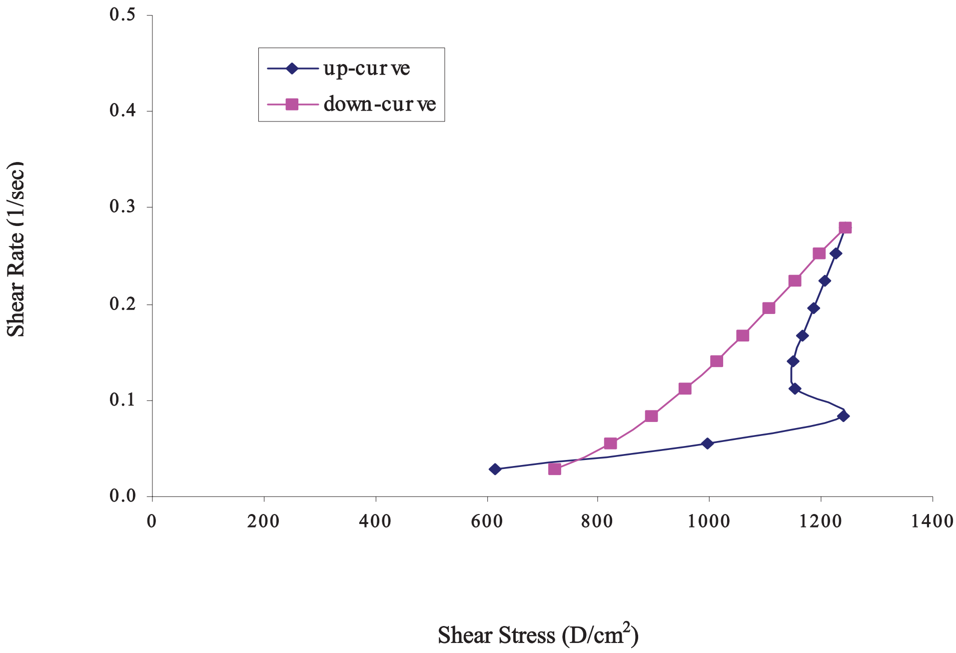

Fig. 6 The effect of added 5% Span 80 on the viscosity of 11% MTS gel base demonstrate a huge hysteresis loop.

Conclusion

The results of the present study indicated that modified starches from Thai local made starches have potential to be utilized as a gelling agent in the gel base. It can be concluded that the physicochemical properties of gel bases achieved from the Thai local made starches were not significantly different from the hydrogel base of semi-synthetic polymer HPMC, which was imported from the other country leading to the promotion of employing Thai local made starches, glutinous starch, rice starch and tapioca starch for making hydrogel instead of semi-synthetic polymer, hydroxypropyl methylcellulose (HPMC).

Acknowledgements

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